PREDICTING PETROLEUM COKE QUALITY FROM FEEDSTOCK PROPERTIES

Joaquín Rodríguez, Carola Acuña,
Jorge Guerrero and León Velasco
Intevep, S.A.PO. BOX 76343
Caracas, Venezuela

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ABSTRACT

A method for predicting petroleum coke quality (Coefficient of Thermal Expansion, CTE) has been developed by correlating feed material properties such as aromatics carbons (wt. %) and optical size texture determined by ^{13}C NMR spectroscopy and polarized light microscopy, respectively.

Correlations used to develop this method are based on characterizations and studies of venezuelan feedstocks such as FCC Decanted Oil, Lube Oil Extract, Flexicoker Recycle Oil and several blends of these materials using the above mentioned analysis, as well as, an evaluation of needle grade coke obtained from the referred feedstocks.

INTRODUCTION

Needle grade coke is a special product obtained from the delayed coking of highly aromatic refinery streams. This special grade coke is used in the fabrication of electrodes for the electric arc furnace in the steel industry. Its a carbonaceous residue of a fibrous nature made up of needle like structures.

Feedstocks used in needle grade coke production are characterized by high aromatic content (>60 wt %), low sulfur content (<1wt %) and a relatively low Conradson Carbon (<10 wt %)[1].

One of the most important properties in assesing needle grade coke quality is the coefficient of thermal expansion (CTE).

In order to determine this property significant amounts of coke are required and pilot plant production of this material becomes necesary.

The fact that coke quality is strongly dependant upon the properties of the feedstock and the operating conditions and therefore on the growth of the mesophase[2,3] which in turn determins the degree of crystallinity of the final product suggests that it should be possible to predict coke quality from feedstock properties at predetermined operating conditions.

The present paper presents the results of the evaluation of a variety of raw materials as potential feedstocks for needle grade coke production. The evaluation includes feedstock characterization by NMR[4], observation of mesophase formation and growth[5] and pilot plant production, calcining and characterization (CTE) of needle grade coke.

The results establish that there is a relationship between the aromatic carbons in the feedstock and the CTE; and between the optical texture size and CTE.

EXPERIMENTAL

NMR spectra of the feedstocks to be evaluated where obtained from a Bruker 300 MSL spectrometer using deuterated chloroform as solvent and TMS as internal reference (0.0 ppm). ^{13}C spectra of the liquid samples were taken at 75.468 MHz and those of ^{1}H at 300 MHz.

Mesophase growth and optical texture size where observed by polarized light microscopy. Samples placed in a micro cell (Figure 1) were subjected to a heat treatment at temperatures between 430°C and 470°C and a H_2 or N_2 pressure up to 2000 psig.

Additionaly the feedstocks were used to produce delayed coke in a 4 litre drum capacity pilot plant with a feedrate between 1500-2000 gr/h, drum internal temp of 400-500°C and two operating pressures (60 and 140 psig).

Green cokes produced were later dried and crushed to 3 mesh in size and after calcined at 850/1250°C.

Several electrode recipies where prepared using the cokes, a coal tar pitch and puffing inhibitors with which 5/8″ diameter and 5″ long bench scale electrodes were made in order to determine the CTE.

RESULTS AND DISCUSSION

Characterization of the feedstocks evaluated (FCC decanted oil, lube oil extract and flexicoker recycle) are shown in table 1. FCC decanted oil subjected to thermal treatment and observed through polarized microscopy exhibits extended fluid domains.

On the other hand flexicoker recycle tends to yield coarse flow mosaics where as Lube Oil Extract due to its low aromaticity gives rise to small mesophase spheres that do not generate mosaics.

Mixture of these feedstocks show intermediate behaviour. Optical texture size depends on the heating rate. Tables 2 and 3 show time of mesophase formation, coalescence period and the optical texture size of the feedstock considered, as well as values of CTE of the needle grade cokes produced from such feedstocks. It can be seen that the optical texture size is inversely proportional to the CTE of the cokes. This suggests that feedstocks that give rise to a greater degree of mesophase development yield higher quality cokes that is, less CTE. Figure 2 illustrates this point. This tendency can be accounted far by the fact that greater degree of mesophase development leads to a greater level of alignment in the aromatic layers which later form a microcrystalline structure that resembles graphite.

Furthermore, a relationship was found between the aromatic carbon content of the feedstock as determined by NMR and the quality of the needle coke. This dependence is shown in Figure 3. No relationship was observed between coke quality and the aromatics content determined by HPLC, which suggests that coke quality does not only depend on the amount of aromatic structures but also the type of structure.

CONCLUSION

Feedstocks evaluation by NMR spectroscopy and polarized light microscopy allows for the quality prediction of needle grade cokes produced at pilot plant scale.

REFERENCES

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TABLE 1. CHARACTERIZATION OF FEEDSTOCKS

PROPERTY	FCCDO	LOE	FCR
API Gravity	6.9	14.6	6.3
KINEMATIC VISCOSITY			
at 60 °C, cSt	61.9	-	-
at 135 °C, cSt		11.0	45.8
Conradson Carbon, wt%	4.26	1.76	15.6
Sulfur, wt%	1.36	2.60	2.77
HPLC fractions, wt%			
Saturates	26.8	25.6	18.2
Aromatics	67.3	69.2	57.1
Polar aromatics	4.7	5.2	18.2
Asphaltenes	1.2	0.0	6.5
^{13}C NMR, wt%			
Parafinic	25.00	42.94	37.41
Naphtenic	22.27	24.76	21.16
Aromatic	52.73	29.30	41.43
-protonated	27.75	11.86	15.54
-quaternary	24.98	17.44	25.89
^{1}H NMR, wt%			
Aliphatic	73.8	64.6	70.3
Aromatic	26.2	35.4	29.7

TABLE 2. EFFECT OF MIXING FCC DECANTED OIL AND FLEXICOKER RECYCLE

FCR wt%	Mesophase formation min.	Coalescence period min.	Size μm	CTE 10^{-7}/C
		20 °C/min. (450°C)		
0	2	5	157	4.1
30	6	10	140	7.3
50	9	12	140	7.6
100	>9	> 17	<50	17.3
		50 °C/min. (450°C)		
0	2	3	250	4.1
30	10	7	380	7.3
50	16	9	<3	7.6
100	9	13	<50	17.3

TABLE 3. EFFECT OF MIXING FCC DECANTED OIL AND LUBE OIL EXTRACT

Lube Oil wt%	Mesophase formation min.	Coalescence period min.	Size μm	CTE 10^{-7}/C
		20 °C/min. (450°C)		
0	2	5	157	4.1
30	3	6	150	5.3
50	na	na	na	7.3
100	no	no	no	na
		50 °C/min. (450°C)		
0	2	3	250	4.1
30	5	no	80	5.3
50	na	na	na	7.3
100	no	no	no	na

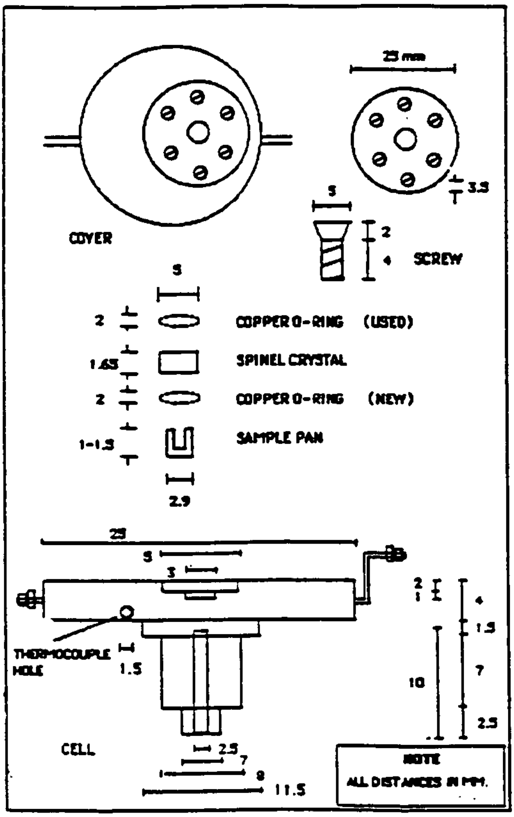

Figure 1. High temperature high pressure micro-cell

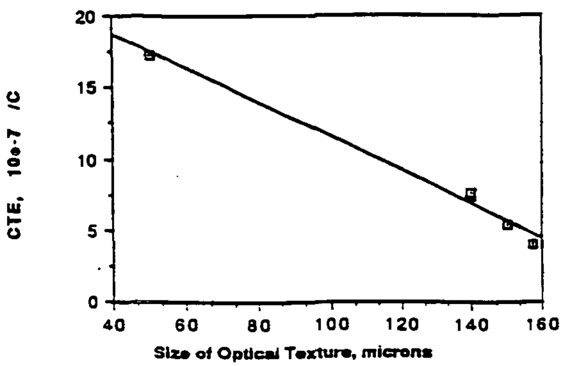

Figure 2.

Relation between Optical Size Texture of mesophase and the Coefficient of Thermal Expansion of cokes

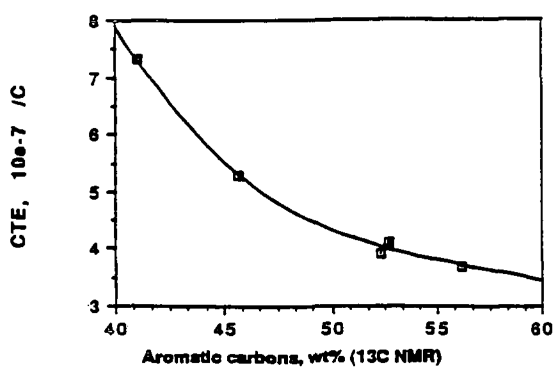

Figure 3.

Relation between NMR characterization of feedstocks and Coefficient of Thermal Expansion of cokes